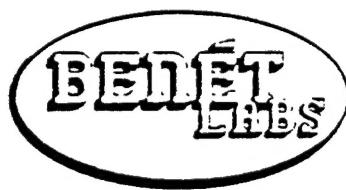# BENÉT INTERNAL TECHNICAL REPORT

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DETERMINATION OF COPPER IN COPPER CYANIDE PLATING SOLUTIONS AND CADMIUM IN CADMIUM CYANIDE PLATING SOLUTIONS BY ATOMIC ABSORPTION SPECTROMETRY

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DETERMINATION OF COPPER IN COPPER CYANIDE PLATING SOLUTIONS AND CADMIUM IN CADMIUM CYANIDE PLATING SOLUTIONS BY ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

The chemical literature lacks specific analytical methods for adequately monitoring copper in copper cyanide plating solutions and cadmium in cadmium cyanide plating solutions during the plating processes. In this report, specific methods are presented that provide acceptable analysis and monitoring of the copper and cadmium in these processes. The optimum operating range of the copper is 16 to 36 g/l in these plating solutions with resulting precisions in the range of 1.3 to 3.0 g/l. The optimum operating range of the cadmium is 17 to 22 g/l in these plating solutions with resulting precisions in the range of 1.3 to 1.8 g/l. Adequate monitoring of these solutions is supported by five years of testing.

KEYWORDS

Chemical Analysis

Copper

Copper Cyanide Plating Solutions

Cadmium

Cadmium Cyanide Plating Solutions

Atomic Absorption Spectrometry

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ACKNOWLEDGMENT

INTRODUCTION

The chemical literature lacks specific analytical methods to adequately monitor copper in copper cyanide plating solutions and cadmium in cadmium cyanide plating solutions during the plating processes. Lack of optimization of these plating solutions causes serious problems for the copper and cadmium plating industry such as poor quality products, wasted human resources, and wasted electrical energy.

The common chemical analysis method to determine copper and cadmium in these plating solutions uses the alkaline precipitation method for these metals (refs 1-2). This method provides adequate precisions but an unacceptable analysis time of two days.

The specific method given in this report provides acceptable analysis and control of copper and cadmium in these plating solutions. The method consists of atomic absorption (AA) spectrometry (ref 3).

EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 1).

Two separate procedures are outlined. The first procedure is for copper in copper cyanide plating solutions and the second procedure is for cadmium in cadmium cyanide plating solutions.

For the copper procedure, one analytical reagent grade standard solution is required. It is a 1.000 ± 0.005-g/l copper solution also containing 50 ml of concentrated nitric acid per liter that meets American Chemical Society (ACS) and American Society For Testing and Materials (ASTM) Standards (ref 4).

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One other reagent grade solution is required. It is concentrated nitric acid.

Three standards are prepared in 500-ml volumetric flasks for AA analysis. The copper concentrations of these are 5.00, 2.50, and 0.00 parts per million (ppm); these standard solutions contain nitric acid for stability.

All copper cyanide plating solution samples are prepared in triplicate in 500-ml volumetric flasks for the copper analysis by this method. A 1:10000 dilution is required of these sample solutions; these sample solutions also contain nitric acid for stability.

The analytical system used is the Perkin-Elmer* AA spectrometer. Reference 4 is an excellent source for the operation and maintenance of this instrument.

The operating conditions for the spectrometer are a 324.8-nm wavelength, 0.7-nm slit size, oxidizing air-acetylene flame, 25 mA-lamp setting, and 2-second integration time.

For the cadmium procedure, one analytical reagent grade standard solution is required. It is a 1.000 ± 0.005-g/l cadmium solution also containing 50 ml of concentrated nitric acid per liter that meets ACS and ASTM Standards (ref 4).

One other reagent grade solution is required. It is concentrated nitric acid.

Three standards are prepared in 500-ml volumetric flasks for AA analysis. The cadmium concentrations of these are 2.00, 1.00, and 0.00 ppm; these standard solutions contain nitric acid for stability.

All cadmium cyanide plating solution samples are prepared in triplicate in 500-ml volumetric flasks for the cadmium analysis by this method. A 1:10000 dilution is required of these sample solutions; these sample solutions also contain nitric acid for stability.

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*Perkin-Elmer Corporation, Norwalk, CT.

The analytical system used is the Perkin-Elmer AA spectrometer. Reference 4 is an excellent source for the operation and maintenance of this instrument.

The operating conditions for the spectrometer are a 228.8-nm wavelength, 0.7-nm slit size, oxidizing air-acetylene flame, 8-mA lamp setting, and 2-second integration time.

Using the procedures in Reference 4, the standard and sample solution absorbance data for copper and cadmium are recorded. Since the standard solution concentrations are known, sample solution concentrations can be calculated.

RESULTS AND DISCUSSION

The calibration data are given for the standard copper and cadmium solutions in Tables IA and IB. The AA spectrometer is linear to 5 ppm copper and 2 ppm cadmium. Also, this instrument is sensitive to 0.1 ppm copper and 0.03 ppm cadmium as shown in the tables. If these data are found to be non-linear, then they must be acquired again.

Tables IIA and IIB present data for copper and cadmium cyanide plating sample solution one, respectively. Tables IIIA and IIIB present data for copper and cadmium cyanide plating sample solution two, respectively. These sample solutions are diluted 1:10000 to attain detector linearity.

Due to a linear operating range, the following simplified calculation is used to determine copper concentation in the original copper cyanide plating sample solutions:

g/l Copper = (50)(sample absorbance/5 ppm standard absorbance)   (1)

The sample one solution in Table IIA has an 18.0-g/l copper concentration and the sample two solution in Table IIIA has a 31.7-g/l copper concentration according to Eq. (1).

Due to a linear operating range, the following simplified calculation is used to determine cadmium concentation in the original cadmium cyanide plating sample solutions:

$$\text{g/l Cadmium} = (20)(\text{sample absorbance}/2 \text{ ppm standard absorbance}) \qquad (2)$$

The sample one solution in Table IIB has an 18.9-g/l cadmium concentration and the sample two solution in Table IIIB has a 19.8-g/l cadmium concentration according to Eq. (2).

It is useful to evaluate the variations in precision for the materials and methods used. Tables IV to XI present these data for the 2.500-ml micropipet, 1.250-ml micropipet, 1.000-ml micropipet, 0.500-ml micropipet, 0.050-ml micropipet, the 500-ml class-A volumetric flasks, the 1.000-g/l copper standard solution, and the 1.000-g/l cadmium standard solution, respectively. Variations in precision are also evaluated for the AA spectrometer. Tables XII and XIII present these data for six consecutive replicates each of the 5.00-ppm copper and 2.00-ppm cadmium standard solutions.

The data by this specific method are sufficient to adequately monitor the copper and cadmium in these cyanide plating processes, thus providing efficient use of resources. The optimum operating range of the copper is 16 to 36 g/l in these plating solutions with resulting precisions in the range of 1.3 to 3.0 g/l. The optimum operating range of the cadmium is 17 to 22 g/l in these plating solutions with resulting precisions in the range of 1.3 to 1.8 g/l. Adequate monitoring of these solutions is supported by five years of testing.

REFERENCES

1. J. Fritz and G. Schenk, <u>Quantitative Analytical Chemistry</u>, Allyn and Bacon, Inc., Boston, MA, 1987.

2. D. Peters, J. Hayes, and G. Hieftje, <u>Chemical Separations and Measurements</u>: <u>Theory and Practice of Analytical Chemistry</u>, W.B. Saunders Company, Philadelphia, PA, 1974.

3. H. Bauer, G. Christian, and J. O'Reilly, <u>Instrumental Analysis</u>, Allyn and Bacon, Inc., Boston, MA, 1978.

4. "AA/ICP Operators Manual," Perkin-Elmer, Inc., Norwalk, CT, 1976.

TABLE IA. STANDARD SOLUTION DATA FOR COPPER

Replicate	Absor. (AU) 0.00 ppm Copper	Absor. (AU) 2.50 ppm Copper	Absor. (AU) 5.00 ppm Copper
1	0.000	0.129	0.256
2	0.000	0.127	0.254
3	0.000	0.127	0.258
X(avg)	0.000	0.128	0.256

TABLE IB. STANDARD SOLUTION DATA FOR CADMIUM

Replicate	Absor. (AU) 0.00 ppm Cadmium	Absor. (AU) 1.00 ppm Cadmium	Absor. (AU) 2.00 ppm Cadmium
1	0.000	0.086	0.178
2	0.000	0.089	0.174
3	0.000	0.089	0.176
X(avg)	0.000	0.088	0.176

**TABLE IIA. EXPERIMENTAL SAMPLE ONE SOLUTION DATA FOR
COPPER IN COPPER CYANIDE PLATING SOLUTIONS**

Replicate	Sample Copper Absor. (AU)	Sample Copper Conc. (ppm)
1	0.095	1.87
2	0.090	1.77
3	0.090	1.77
X(avg)	0.092	1.80

**TABLE IIB. EXPERIMENTAL SAMPLE ONE SOLUTION DATA FOR
CADMIUM IN CADMIUM CYANIDE PLATING SOLUTIONS**

Replicate	Sample Cadmium Absor. (AU)	Sample Cadmium Conc. (ppm)
1	0.165	1.87
2	0.167	1.90
3	0.168	1.91
X(avg)	0.167	1.89

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TABLE IIIA. EXPERIMENTAL SAMPLE TWO SOLUTION DATA FOR COPPER IN COPPER CYANIDE PLATING SOLUTIONS

Replicate	Sample Copper Absor. (AU)	Sample Copper Conc. (ppm)
1	0.162	3.18
2	0.159	3.13
3	0.163	3.20
X(avg)	0.161	3.17

TABLE IIIB. EXPERIMENTAL SAMPLE TWO SOLUTION DATA FOR CADMIUM IN CADMIUM CYANIDE PLATING SOLUTIONS

Replicate	Sample Cadmium Absor. (AU)	Sample Cadmium Conc. (ppm)
1	0.175	1.99
2	0.175	1.99
3	0.172	1.95
X(avg)	0.174	1.98

TABLE IV. PRECISION OF MICROPIPETTING 2.500 ml

Replicate	Volume (ml)*
1	2.531
2	2.505
3	2.484
4	2.501
5	2.525
6	2.477
X(avg)	2.504
Sn	0.021

*Volumes are calculated from the weight-volume relationship
of each micropipetted deionized water solution corrected
for temperature.

TABLE V. PRECISION OF MICROPIPETTING 1.250 ml

Replicate	Volume (ml)*
1	1.249
2	1.239
3	1.263
4	1.246
5	1.256
6	1.252
X(avg)	1.251
Sn	0.008

*Volumes are calculated from the weight-volume relationship
of each micropipetted deionized water solution corrected
for temperature.

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TABLE VI. PRECISION OF MICROPIPETTING 1.000 ml

Replicate	Volume (ml)*
1	1.0133
2	1.0105
3	1.0140
4	1.0066
5	1.0106
6	1.0065
X(avg)	1.0102
Sn	0.0029

*Volumes are calculated from the weight-volume relationship
of each micropipetted deionized water solution corrected
for temperature.

TABLE VII. PRECISION OF MICROPIPETTING 0.500 ml

Replicate	Volume (ml)*
1	0.4987
2	0.4998
3	0.5012
4	0.4999
5	0.5014
6	0.5003
X(avg)	0.5002
Sn	0.0010

*Volumes are calculated from the weight-volume relationship
of each micropipetted deionized water solution corrected
for temperature.

TABLE VIII. PRECISION OF MICROPIPETTING 0.050 ml

Replicate	Volume (ml)*
1	0.0494
2	0.0508
3	0.0533
4	0.0522
5	0.0497
6	0.0517
X(avg)	0.0512
Sn	0.0015

*Volumes are calculated from the weight-volume relationship of each micropipetted deionized water solution corrected for temperature.

TABLE IX. PRECISION OF 500-ml CLASS-A VOLUMETRIC FLASK

Replicate	Volume (ml)*
1	500.6
2	500.1
3	499.8
4	500.0
5	500.5
6	499.3
X(avg)	500.1
Sn	0.4

*Volumes are calculated from the weight-volume relationship of the contained deionized water solution corrected for temperature.

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TABLE X. PRECISION OF 1.000-g/l COPPER STANDARD SOLUTION

Replicate	Copper Conc. (g/l)*
1	1.001
2	0.994
3	0.996
4	1.005
5	1.004
6	0.997
X(avg)	1.000
Sn	0.005

*Copper concentrations are determined by the alkaline
precipitation method in References 1 and 2 which is a
standard chemical analysis method for copper.

TABLE XI. PRECISION OF 1.000-g/l CADMIUM STANDARD SOLUTION

Replicate	Cadmium Conc. (g/l) *
1	1.006
2	1.003
3	0.993
4	0.999
5	1.007
6	0.999
X(avg)	1.001
Sn	0.005

*Cadmium concentrations are determined by the alkaline
precipitation method in References 1 and 2 which is a
standard chemical analysis method for cadmium.

**TABLE XII.   PRECISION OF 5.00-ppm COPPER STANDARD
SOLUTION BY AA SPECTROMETRY**

Replicate	Absor. (AU) 5.00 ppm Copper
1	0.256
2	0.254
3	0.258
4	0.259
5	0.258
6	0.255
X(avg)	0.257
Sn	0.002

**TABLE XIII.   PRECISION OF 2.00-ppm CADMIUM STANDARD
SOLUTION BY AA SPECTROMETRY**

Replicate	Absor. (AU) 2.00 ppm Cadmium
1	0.178
2	0.174
3	0.176
4	0.176
5	0.178
6	0.177
X(avg)	0.177
Sn	0.002

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